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THERMAL AND TRANSPORT PROPERTIES

OF

GRANULAR METAL THIN FILMS

Final Report

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Submitted by

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Introduction

The objectives of our research program have been to carry out a systematic experimental and theoretical study of the thermal and transport properties of granular metal films. This work has involved the preparation of a number of different granular metal systems by RF sputter deposition, characterization of these materials by x-ray diffraction (XRD), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS), the study of thermal properties by differential scanning calorimetry (DSC) measurements, and the study of the electrical transport behavior from room temperature to below 100 mK and, at low temperatures, in applied magnetic fields up to about 6 T. Using a variety of complementary analytical and numerical techniques, detailed theoretical studies have also been carried out on the structure, melting, transport, and optical properties of small granular particles. The major results of these efforts are presented in the following sections, and have been described in detail in the 21 papers that have appeared in referred journals, one book chapter, and two patents arising from this work.

Structure

The stucture of the granular metal films studied in this work has been found to be generally consistent with previous studies.[1] When deposited onto fixed temperature substrates, the mean particle size generally becomes smaller and the size distribution more uniform as the metal composition is reduced. Low melting point metals have been found to form larger particles with a wider distribution of sizes than do higher melting point metals prepared at the same composition.[2,3] These features are illustrated in the TEM micrographs of $Ni_x(SiO_2)_{100-x}$ and $Sn_x(SiO_2)_{100-x}$ granular films shown in Figs. 1 and 2. At a fixed metal composition, the particle size depends on the substrate temperature[4] with higher substrate temperatures resulting in larger and more uniform particle sizes as shown in Fig. 3. The details of the mean particle size and the particle size distribution depend on the actual metal/insulator combination.

In most granular metal systems the bulk metal structure is retained in the small particles, albeit with size dependent lattice parameters. Figure 4 shows the evolution of the "c" lattice parameter of rhombohedral Bi (indexed on a hexagonal cell) with particle size and substrate temperature. While the general trend is towards a larger "c" parameter with decreasing particle size, it is interesting to note that the smallest measured particles appear to exhibit a contracted lattice parameter. The "a" lattice parameter, on the other hand, remains essentially unchanged. A similar lattice expansion has also been observed in small Fe particles.[5]

The structure of small metallic particles has been studied theoretically based on the self-consistent Einstein model with a Morse interaction potential.[6] This calculation predicts an expanded lattice with decreasing particle size. Associated with the expanded lattice, the Debye temperature drops significantly for particles smaller than about 50 Å in size. The theoretically calculated size dependence of the lattice parameter in the case of small Fe particles is shown in Fig. 5. A reduced Debye temperature, in reasonable agreement with the predicted value, has recently been observed in a Mossbauer effect experiment.[5]

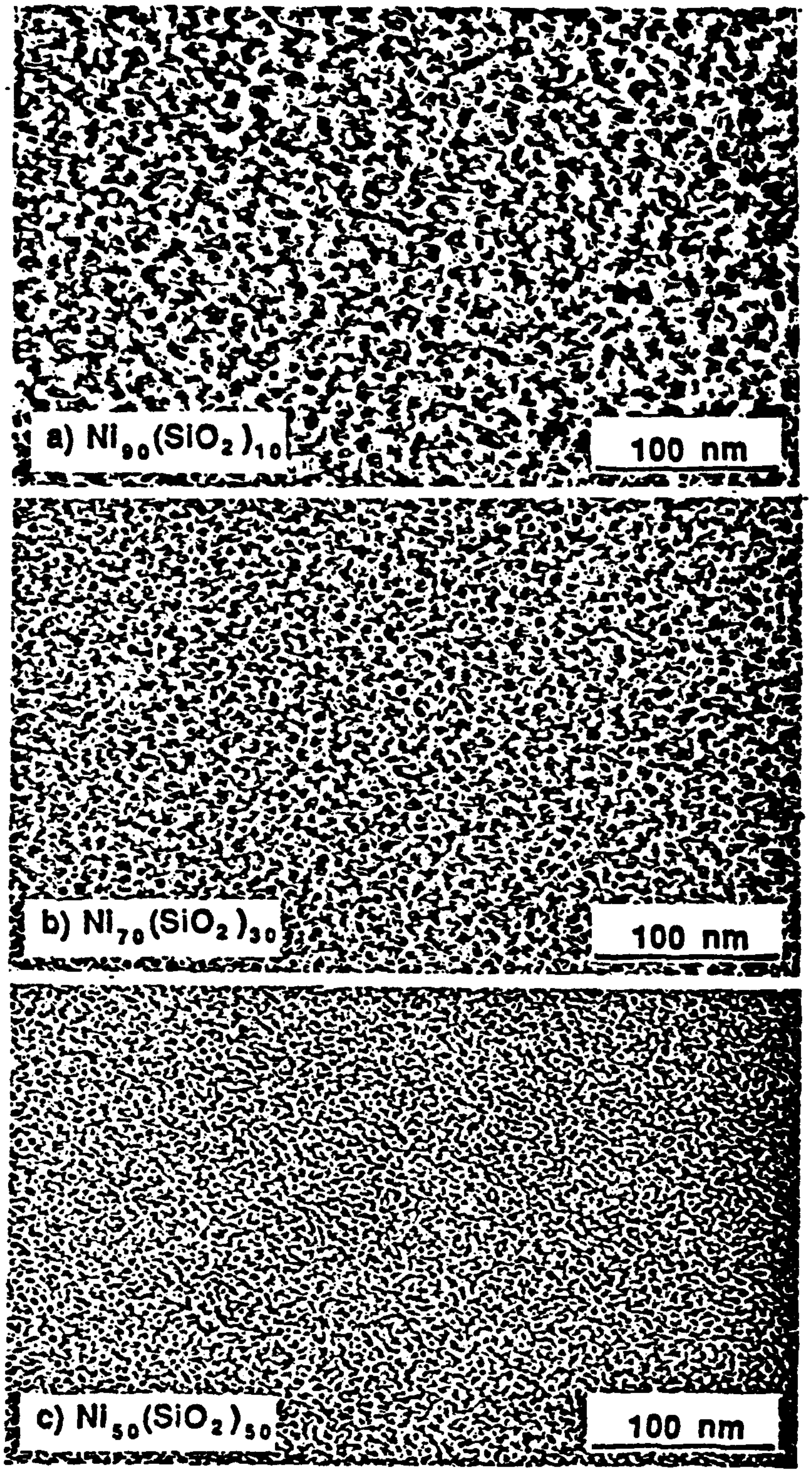


Fig. 1: TEM micrographs of granular $Ni_x(SiO_2)_{100-x}$ films for Ni concentrations of $x=90$, 70, and 50 atomic percent.

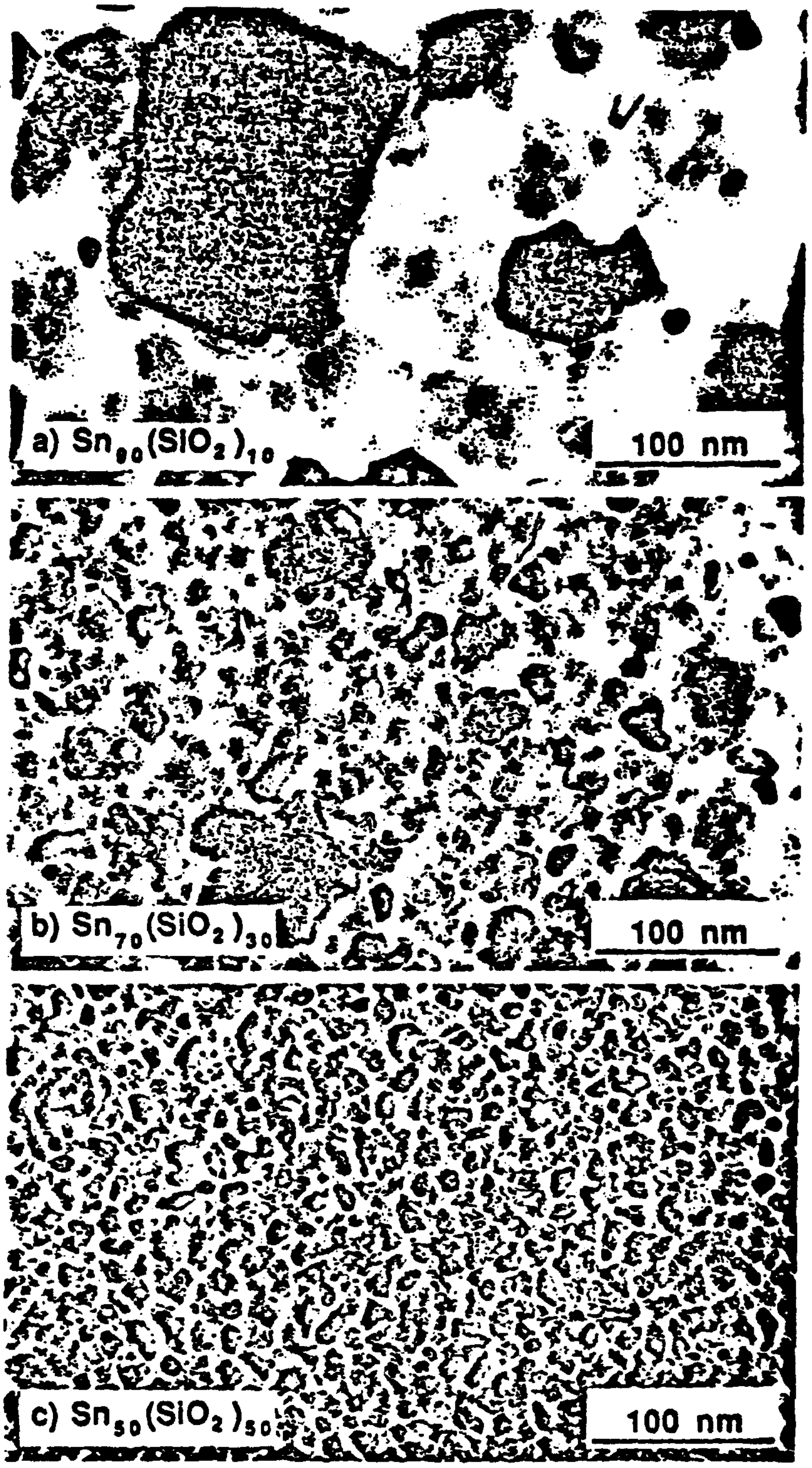


Fig. 2: TEM micrographs of granular $Sn_x(SiO_2)_{100-x}$ films for Sn concentrations of $x=90$, 70, and 50 atomic percent.

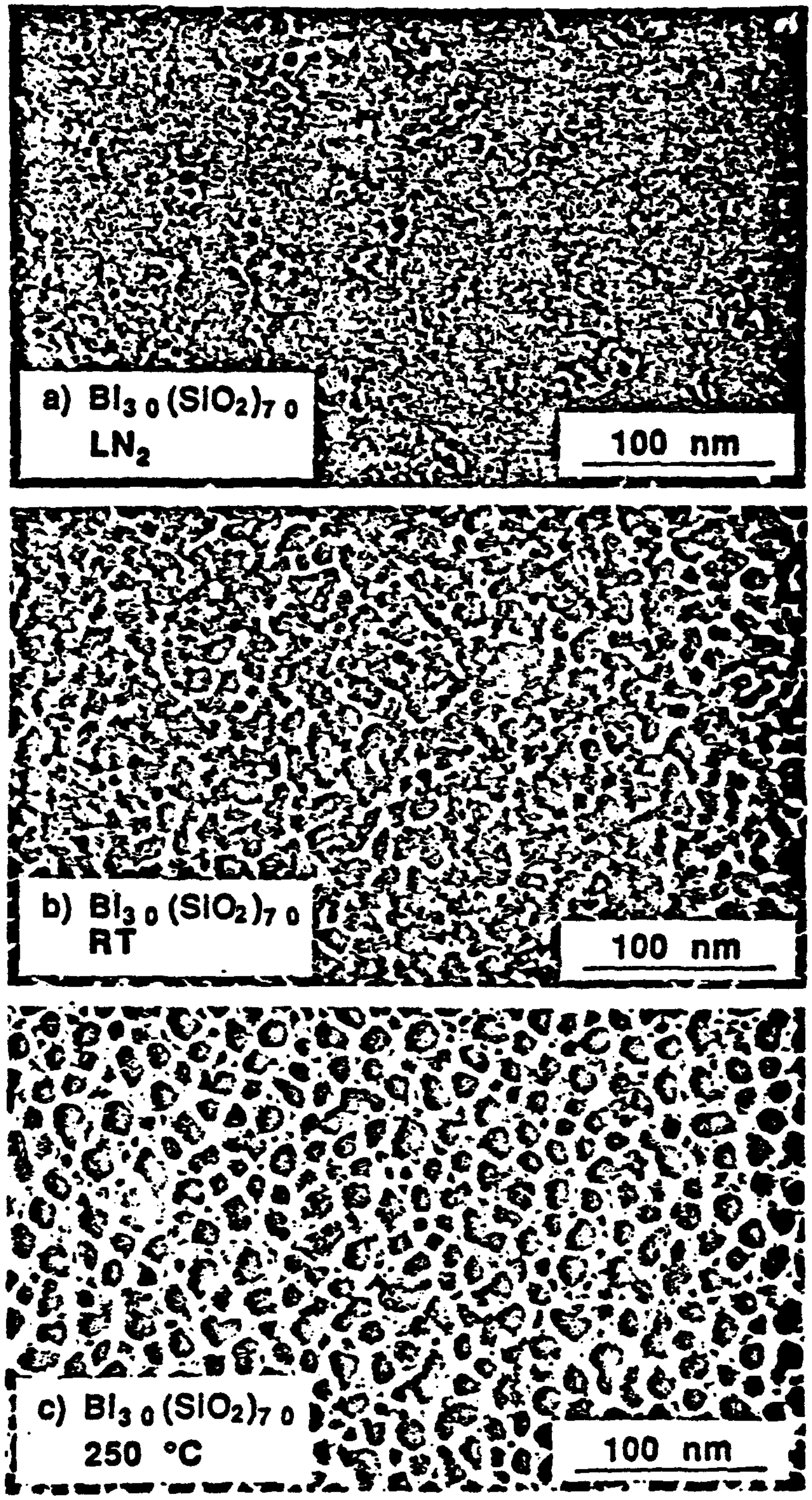


Fig. 3: TEM micrographs of granular $Bi_{30}(SiO_2)_{70}$ films deposited on substrates at LN_2, room temperature, and 250 °C.

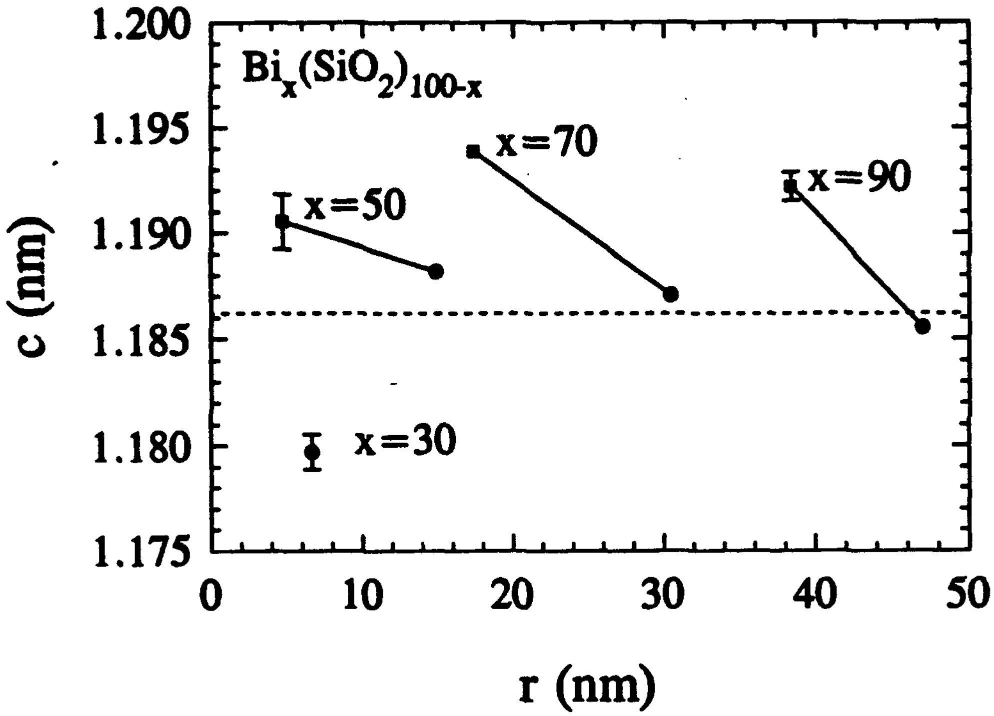


Fig. 4: Evolution of the Bi "c" lattice parameter with particle radius. Squares correspond to LN_2 cooled substrates and circles to 250 °C substrates. The dashed line is the bulk c parameter.

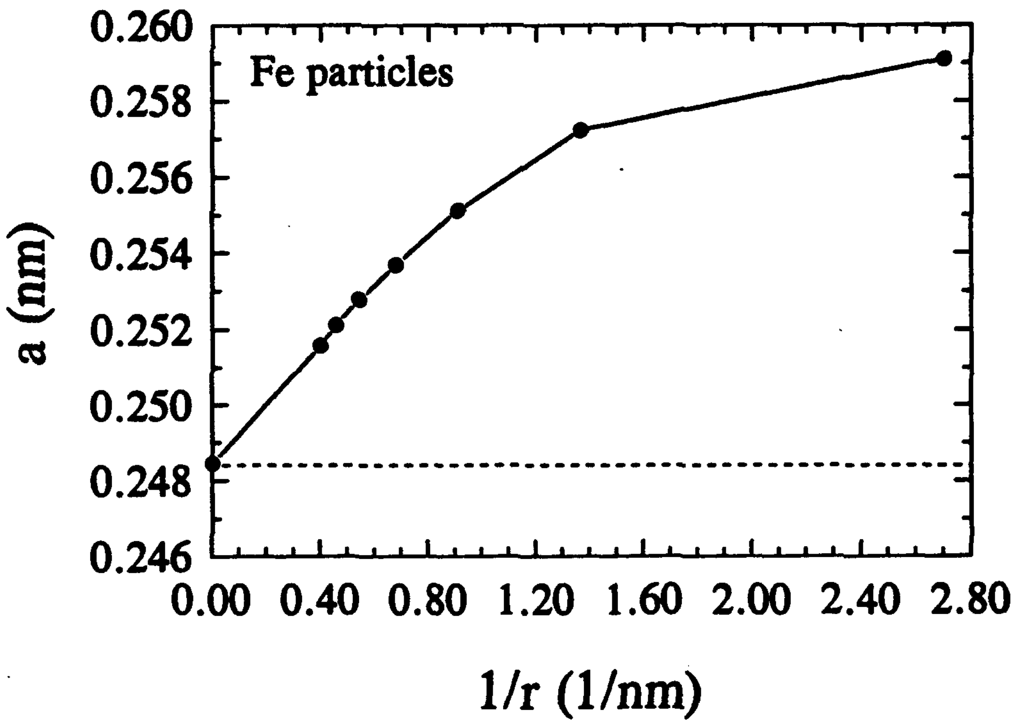


Fig. 5: Theoretically calculated lattice parameter "a" of small Fe particles as a function of reciprocal particle radius. The dashed line is the bulk a parameter.

Finally, as shown in Fig. 6, W particles in the W-SiO_2 granular system do not exhibit the bulk α-W BCC structure, but rather the β-W A15 structure. This structure has also been observed in thin, RF sputtered, W films where the β-W phase has been found to be relatively unstable, transforming to α-W at a temperature of only about 135 °C.[7] In the form of small particles in an SiO_2 matrix, however, the β-W phase is retained even following a 600 °C anneal for several hours.

Thermal Properties

Interest in the melting behavior of very small particles arises from several different considerations. The microscopic nature of the solid-liquid melting transition in bulk matter, despite considerable experimental and theoretical effort, remains an incompletely understood phenomenon. In addition, finite size effects lead to strong modifications of bulk melting properties. A number of theoretical treatments of the solid-liquid transition in free particles of finite size now exist,[8] and the study of small particles offers the opportunity to compare theory and experiment. When the effects of a confining matrix are included, additional corrections to the bulk melting temperature are expected.[6,9] Granular metal films are well suited for these studies.

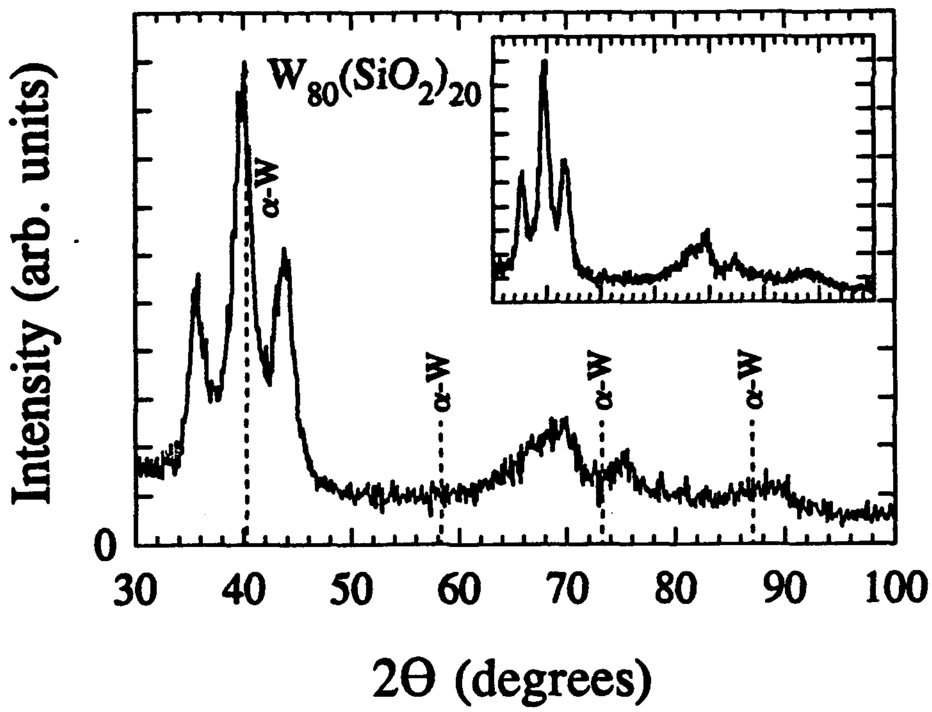


Fig. 6: XRD pattern of an as-deposited granular $W_{80}(SiO_2)_{20}$ film and (insert): the same film annealed at 600 °C for 2 hours. The diffraction lines correspond to β-W (the dashed lines indicate the peak positions of α-W).

The solid-liquid and liquid-solid transitions in granular metal films of In, Pb, Sn, and Bi in SiO_2 and Al_2O_3 matrices have been systematically studied as a function of metal particle size and volume fraction.[2,4,10] In the case of the solid-liquid transition, the melting temperature of small metal particles has been observed to be increasingly depressed with respect to the bulk value as the particle size is reduced. This effect is illustrated in Fig. 7 for the case of small Bi particles in a SiO_2 matrix. The solid line drawn through the data points is a best fit to the first order correction to the melting temperature of free spherical particles described in the following paragraph.

Melting point depressions in small particles are expected on the basis of classical thermodynamic treatments of melting. These theoretical treatments predict a size dependent melting temperature $T_m(r)$, reduced from the bulk value T_0 by an amount

$$T_m(r) = T_0(1 + \alpha r^1 + \beta r^2 + \cdots) \quad (1)$$

where α and β depend on material properties and the precise melting criterion adopted.[10] The constant α is typically negative so Eq. 1 predicts size dependent melting temperature reductions as shown in Fig. 7. Thermodynamic treatments of melting, while straightforward and intuitive do not, however, offer microscopic insight into the melting process.

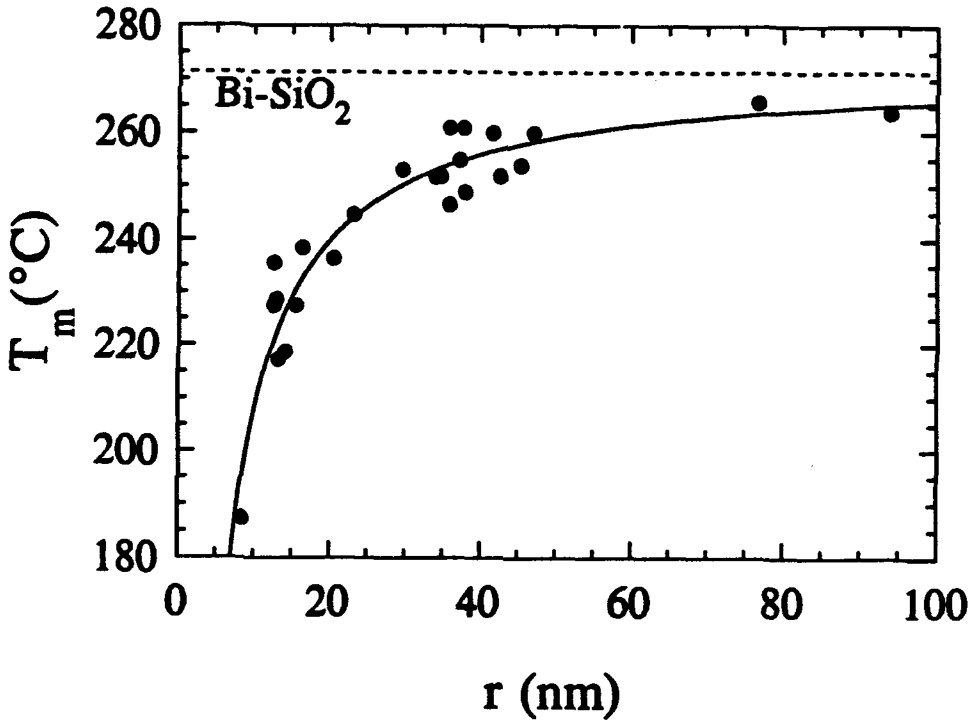


Fig. 7: Melting temperature of Bi particles in granular $Bi_x(SiO_2)_{100-x}$ films as function of the particle radius. The solid line is a best fit to the first order term of Eq. 1, and the dashed line is the melting temperature of bulk Bi.

In order to obtain more detailed theoretical information on the solid-liquid transition, microscopic calculations have been carried out.[6] This work has been based on the self-consistent Einstein model using a generalized Lindemann criterion for melting, and on a generalized Lennard-Jones-Devonshire cell model. Similar melting point depressions have been obtained with both models. In addition, the normalized melting temperature $T_m(r)/T_0$ has been found to be insensitive to lattice structure and exhibits a nearly universal behavior. Figure 8 illustrates the size dependence of the normalized melting temperature in the case of small Fe particles. Unfortunately, due to computational difficulties, the largest particles studied theoretically barely overlap with the smallest particles studied experimentally. In the limited overlap region, however, the calculations are in reasonable agreement with experiment.

The liquid-solid freezing transition is an activated process which requires the formation of a critically sized nucleus in the undercooled melt. Heterogeneous nucleation on impurities is generally more favorable energetically than homogeneous nucleation and makes large undercoolings difficult to obtain in bulk matter. In order to limit the heterogenous nucleation of the solid on impurities, Turnbull devised a method of studying nucleation in finely divided particles where the probability of finding impurity free particles was large.[11] More recently, this basic technique has been extended by others.[12] In each case, however, sample preparation methods rarely produced particles less than about one μm in size.

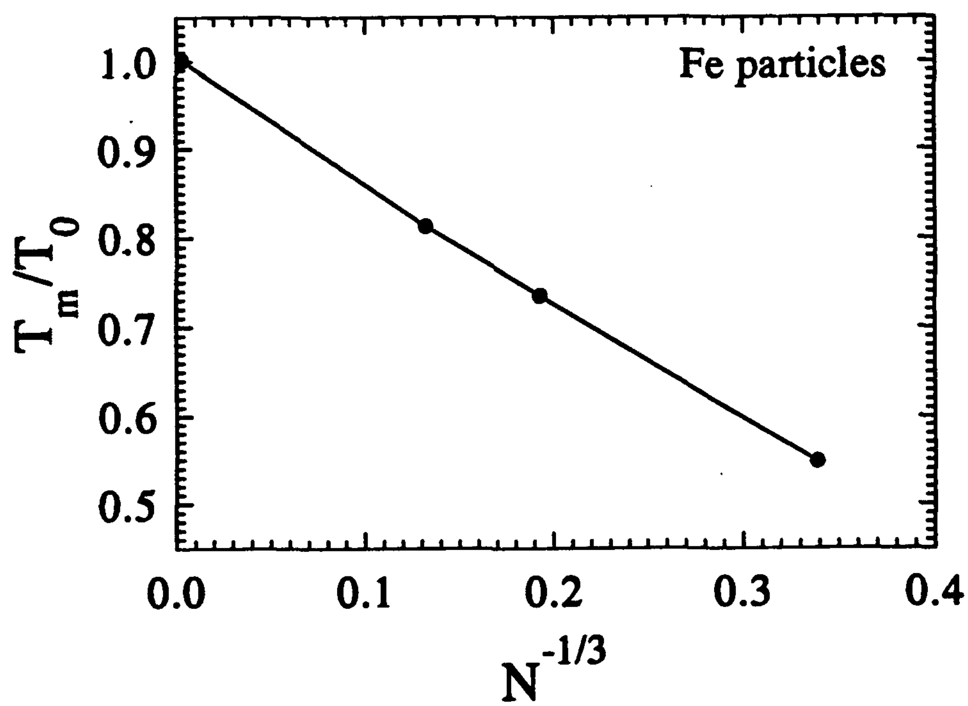


Fig. 8: Normalized melting temperature of Fe as a function of $N^{-1/3}$ (N is the number of atoms in the particle).

We have studied the freezing behavior of small Sn and Bi particles embedded in SiO_2 matrices. As expected, large undercoolings have been obtained. In Bi particles deposited on substrates heated to near the bulk Bi melting temperature, undercoolings of greater than 30 percent have been obtained at cooling rates of 10 °C/min. The small size of these particles has also allowed the observation of strong fluctuations in the freezing temperature.

Transport Properties

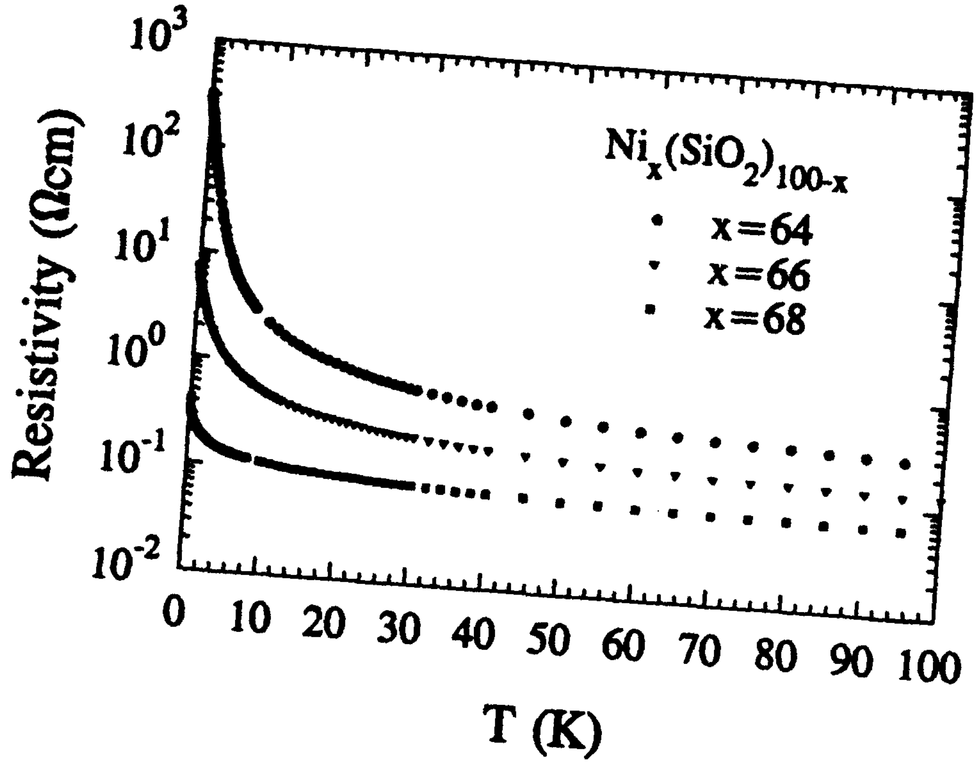
Granular metal films offer an opportunity to explore fundamental questions about the role of disorder and finite particle size in electrical transport. By controlling the individual particle size and the metal volume fraction the electrical properties of granular metal films can be continuously "tuned" from metallic to insulating. It has recently been recognized that granular metal films also provide an opportunity to study the connection between superconductivity and the metal-insulator transition in two and three dimensions.[13]

A systematic study of the temperature and applied magnetic field dependence of the resistivity in the granular $Ni_x(SiO_2)_{100-x}$ system has been carried out from room temperature to below 100 mK and, at low temperatures, in fields up to about 6 T.[14,15] The resistivity results are summarized in Figs. 9 through 11. The range of compositions studied spans the range from insulating to metallic behavior. Film compositions corresponding to about x=70 atomic percent mark the boundary between insulating and metallic samples in the sense that those films with Ni concentrations less than 70 atomic percent exhibit negative temperature coefficients of resistivity (TCR) at room temperature (see Fig. 9), while those films with larger Ni concentrations exhibit positive TCR's (see Fig. 10). In the insulating regime the temperature dependence of the resistivity, between room temperature and about 5 K, can be well described by an expression of the form

$$\rho(T) = \rho_0 \exp[(T_0/T)^{1/2}] \tag{2}$$

where $T_0=T_0(x)$ is an increasing function of x as has been discussed previously.[1,16] Below 1 K the resistivity of all these films is independent of composition and is weaker than Eq. 2. A possible mechanism for this unexpected behavior has been proposed.[17] This property also makes these materials attractive as cryogenic temperature sensors.[14] All samples in the metallic regime have a resistance minimum below which the resistivity $\rho(T)$ increases logarithmically with temperature.

When the resistivity of the granular $Ni_x(SiO_2)_{100-x}$ films is measured in an applied transverse magnetic field the magnetoresistance is found to be small and negative at all temperatures. The largest observed changes were about 2 percent, measured in a field of 6 T and at a temperature of 0.2 K. The magnetoresistance saturates at fields above about 2 T. These properties are illustrated in Fig. 11. In conjunction with the temperature dependence described above, the weak magnetoresistance is also a desirable property for high field thermometry.



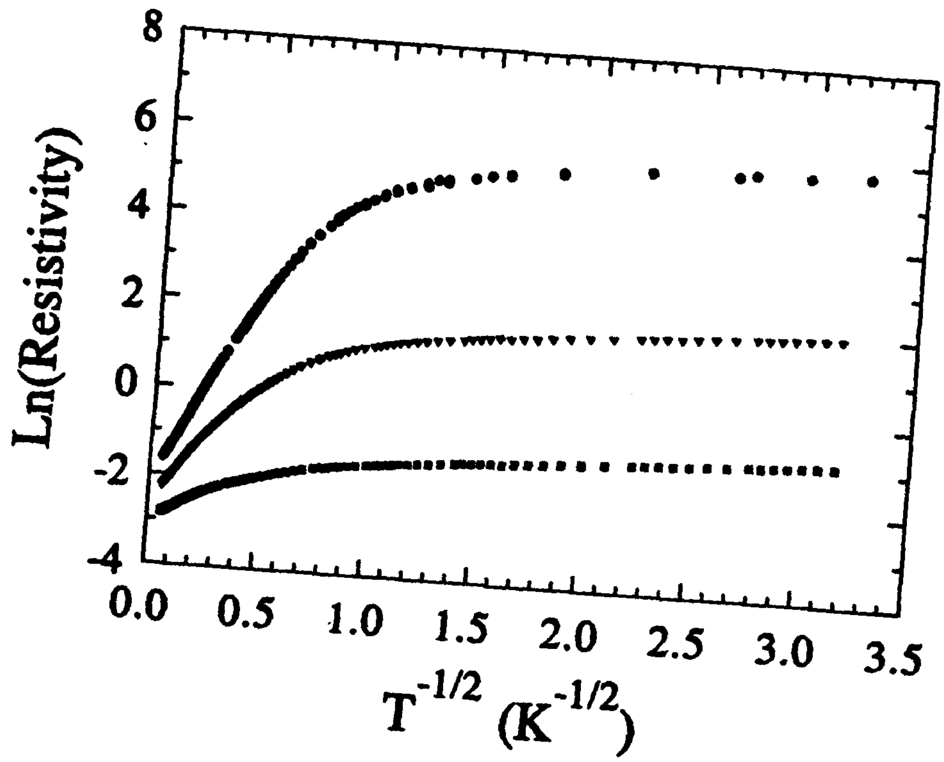


Fig. 9: Transport behavior of several typical $Ni_x(SiO_2)_{100-x}$ granular films in the insulating regime as a function of composition and temperature.

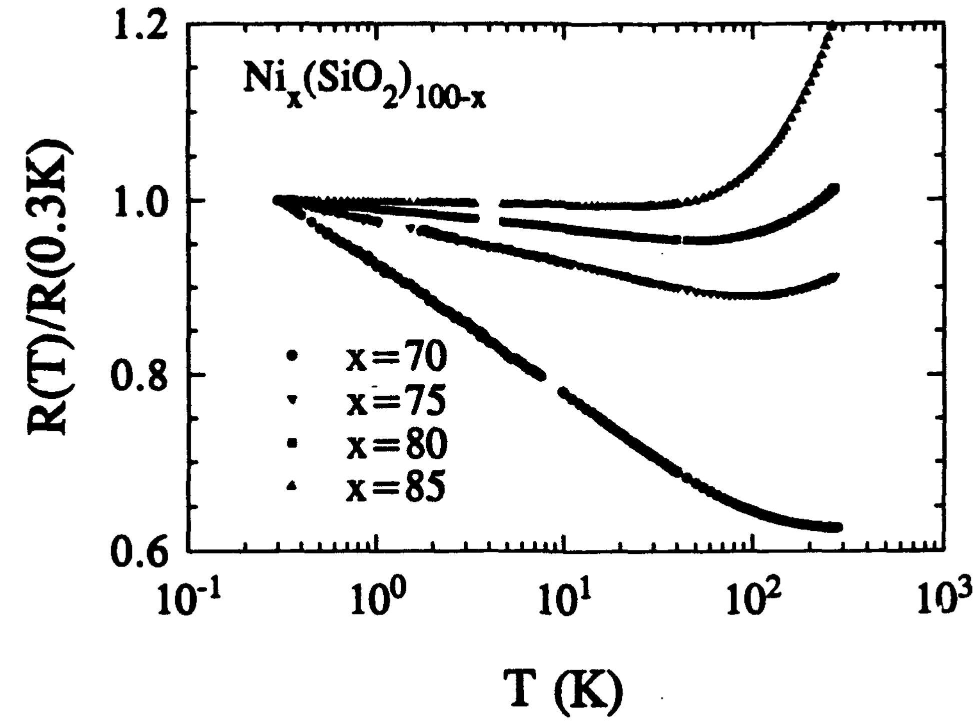


Fig. 10: Transport behavior of several typical $Ni_x(SiO_2)_{100-x}$ granular films in the metallic regime as a function of composition and temperature.

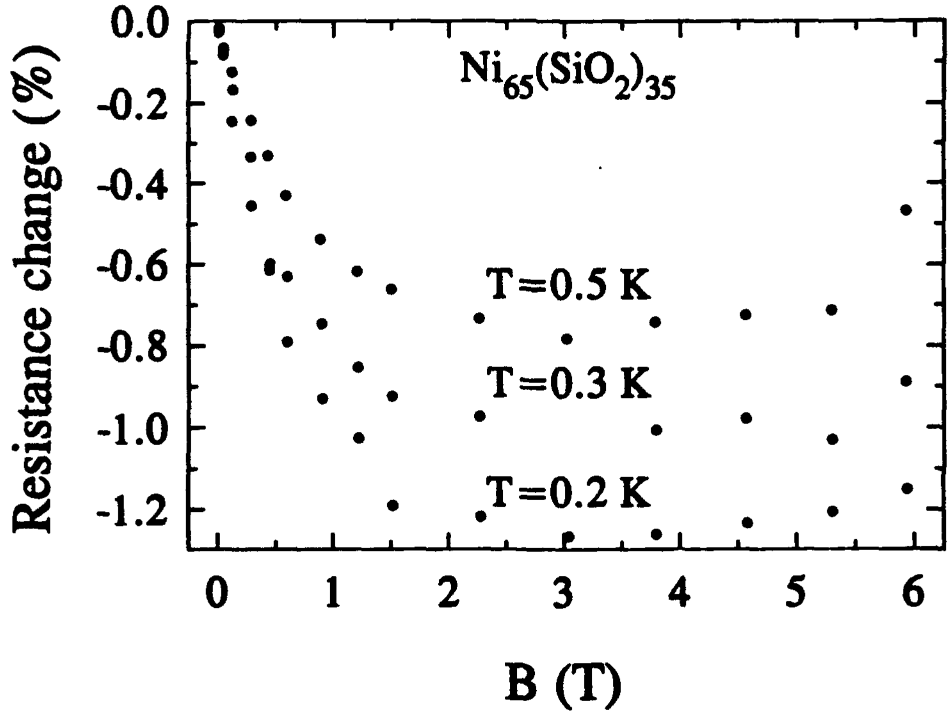


Fig. 11: Magnetoresistance of a granular $Ni_{65}(SiO_2)_{35}$ film as a function of temperature and applied magnetic field.

We have also carried out transport measurements on several other granular systems, including Ni-Al_2O_3, Cu-SiO_2, and W-SiO_2. These films all exhibit a crossover from metallic to insulating behavior with decreasing metal fraction. However, their low temperature transport behavior in the insulating regime is rather different from that of the Ni films. In particular, the magnetoresistance changes sign from positive above 0.5 K to negative at lower temperatures. This behavior is consistent with theoretical work by Sheng.[18]

The transport properties of granular $Sn_x(SiO_2)_{100-x}$ films have also been studied,[19] and at temperatures above about 5 K were found to be qualitatively similar to the previously studied Ni-SiO_2 system. The boundary between metallic and insulating films, for example, occured at Sn composition between 55 and 60 atomic percent. Below 5 K, compositions with $x \geq 55$ atomic percent become superconducting with slightly enhanced transition temperatures in comparison with bulk Sn. When the superconducting transition is suppressed by the application of a magnetic field in the metallic Sn films, a minimum in the resistivity is observed followed by an increase in the resistivity proportional to ln(T) at lower temperatures. Interestingly, a x=55 atomic percent film also becomes superconducting despite the fact that its normal state resistivity is more characteristic of an insulator than a metal as shown in Fig. 12. In fact, the resistivity of this film at the onset of superconductivity is somewhat larger than the largest resistivity for which superconductivity has been observed in granular Al.[13]

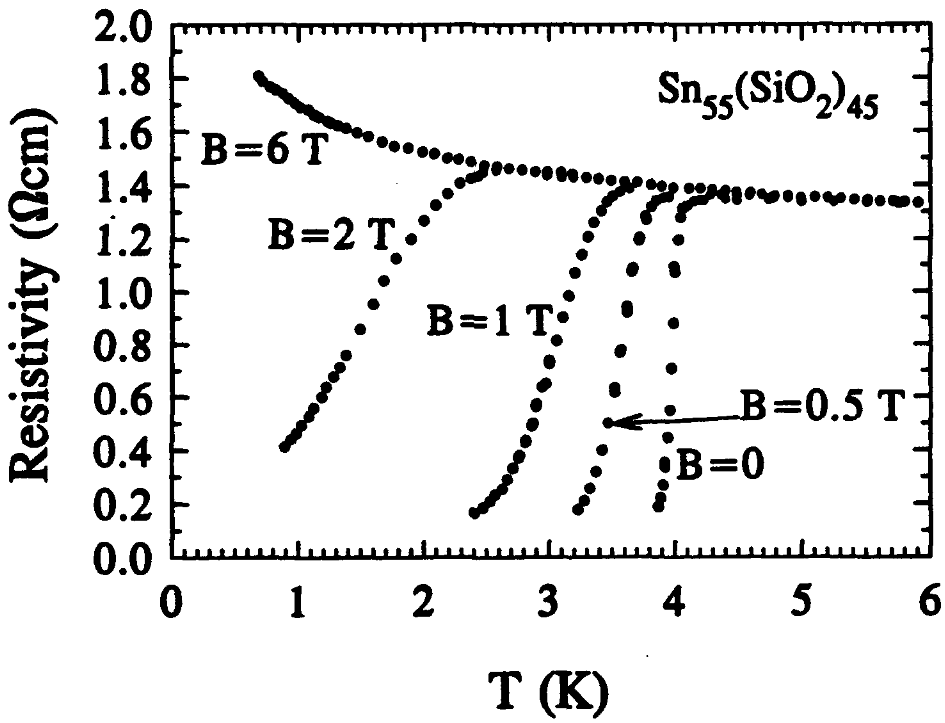


Fig. 12: Resistivity of a $Sn_{55}(SiO_2)_{45}$ granular film as a function of temperature and applied magnetic field B.

Infrared Properties

A key feature of composite materials in general, and granular metals in particular, is the possibility of tuning their physical properties through microstructural control. From the standpoint of optical properties, broad size and shape distributions currently limit novel applications of these materials. However, as more sophisticated fabrication techniques become available, detailed theoretical studies of structure specific optical properties are increasingly important.

We have completed a theoretical study of the infrared properties of a new class of structured small particles.[20] Compared to the particles in a granular metal, these particulates are structured in the sense that they consist of a metal-insulator superlattice of modulation period l_0, width d, and height L. By varying both the superlattice period and particle dimensions the optical absorption properties can be controlled. A schematic representation of such a particle is illustrated in Fig. 13. These particulates exhibit novel optical properties when infrared radiation is incident on their exposed layered facets. In the narrow particle limit, a series of sharply defined absorption peaks at frequencies controlled by the width has been found. In the wide particle limit most of the incident radiation will be absorbed, resulting in a broad band absorber. The absorption behavior of a structured Cu-Ge particulate in the narrow particle limit is shown in Fig. 14. The infrared absorption of these materials is an order of magnitude larger than that of doped semiconductors.

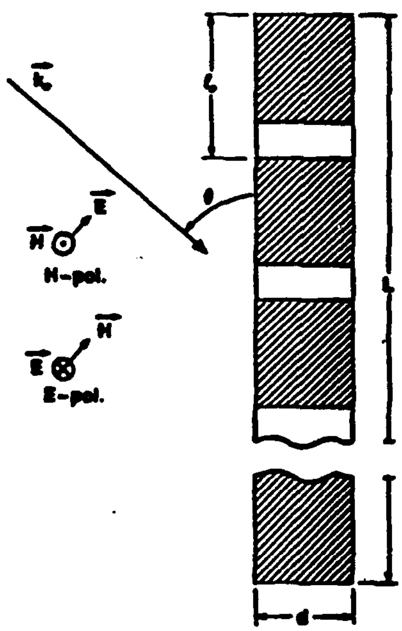


Fig. 13: Schematic representation of a structured metal-insulator particulate. The two field configurations of incident radiation with wave vector k_0 are also shown.

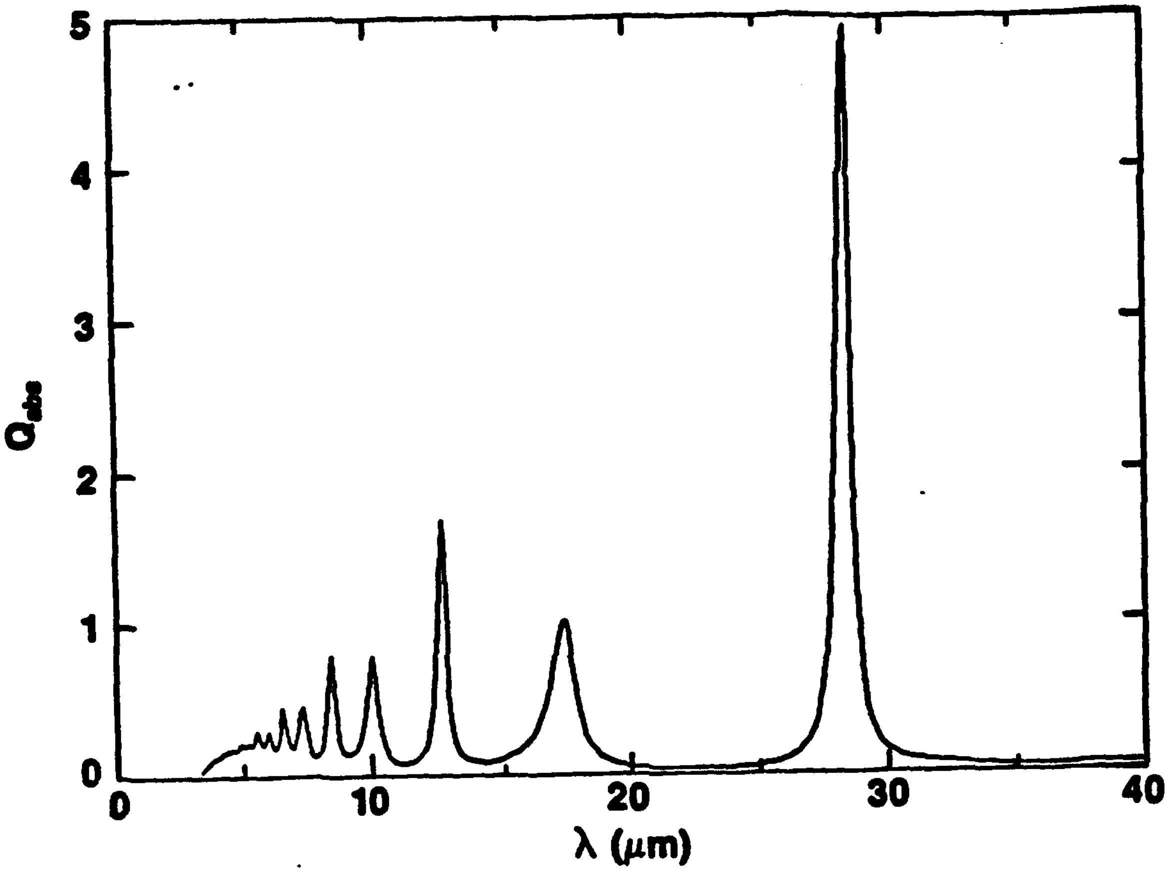


Fig. 14: Calculated orientational and polarization averaged absorption efficiency of a structured Cu-Ge particulate with metal fraction p=.967 and d=2μm as a function of wavelength.

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3. Patents

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Cryogenic Resistance Thermometer Comprising a Granular Nickel in Silica Film.

2. S.-T. Chui, P. Sheng, K.M. Unruh, and G. Watson, our patent application for using structured granular materials as infrared absorbers has been allowed but was not registered because it was placed under a secrecy order (07-640-144) by the government.
   Structured Granular Metals

4. Invited Presentations

1. K.M. Unruh and B.M. Patterson, presented at the Spring Meeting of the Materials Research Society, San Francisco, CA 1990.
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5. Contributed Presentations

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2. P. Sheng, M.-Y. Zhou, Z. Chen, and S.-T. Chui, presented at the Fall Meeting of the Materials Research Society, Boston, MA 1988.
   Optical Properties of Finely Structured Particulates.

3. K.M. Unruh, B.M. Patterson, N. Mulders, C. Swann, and J.R. Beamish, presented at the March Meeting of the American Physical Society, St. Louis, MO 1989.
   Preparation and Transport Properties of Reactively Sputtered ZrN_x.

4. J.R. Beamish, K.M. Unruh, and B.M. Patterson, presented at the March Meeting of the American Physical Society, Anaheim CA 1990.
   Electrical Resistivity of Granular Nickel Films.

5. K.M. Unruh, B.M. Patterson, J.R. Beamish, Li Yiping, and G.C. Hadjipanayis, presented at the March Meeting of the American Physical Society, Anaheim CA 1990.
   Magnetic Properties and Magneto-resistance of Granular Metal Films.

6. B.M. Patterson, K.M. Unruh, and J.R. Beamish, presented at the March Meeting of the American Physical Society, Anaheim CA 1990.
   Melting and Freezing Behavior of Small Bi Particles in Granular Bi-SiO_2 Films.

7. Z.-Q. Zhang and P. Sheng, presented at the March Meeting of the American Physical Society, Anaheim CA 1990.
   Theoretical Calculations of Magnetoresistance in Granular Metal Films.

8. M.-Y. Zhou and P. Sheng, presented at the March Meeting of the American Physical Society, Anaheim CA 1990.
   Melting and Thermal Characteristics of Small Particles Embedded in an Elastic Matrix.

9. S.-T. Chui, presented at the March Meeting of the American Physical Society, Anaheim CA 1990.
   Melting of Clusters and Films as a Mass Density Wave Instability.

10. J.R. Beamish, B.M. Patterson, and K.M. Unruh, presented at the Spring Meeting of the Materials Research Society, San Francisco, CA 1990.
    Superconductivity in Granular $Sn_x(SiO_2)_{100-x}$ Thin Films.

11. J.R. Beamish, B.M. Patterson, and K.M. Unruh, presented at the Spring Meeting of the Materials Research Society, San Francisco, CA 1990.
    Transport Properties of Granular $Ni_x(SiO_2)_{100-x}$ Thin Films.

12. Z.-Q. Zhang and P. Sheng, presented at the Spring Meeting of the Materials Research Society, San Francisco, CA 1990.
    A Quantum Percolation Model for Magnetoconductance of Granular Metal Films.

13. L.F. Chen, P. Sheng, B. Abeles, and M.-Y. Zhou, presented at the Spring Meeting of the Materials Research Society, San Francisco, CA 1990.
    Numerical Simulation of Hopping Conductivity in Granular Metal Materials.

14. P. Sheng and M.-Y. Zhou, presented at the Spring Meeting of the Materials Research Society, San Francisco, CA 1990.
    Melting and Thermal Characteristics of Small Granular Particles.

15. Z.-Q. Zhang and P. Sheng, presented at the March Meeting of the American Physical Society, Cincinnati, OH 1991.
    Superdiffusive Transport and Metal-Insulator Transition in 2D.

16. P. Sheng and Z.-Q. Zhang, presented at the March Meeting of the American Physical Society, Cincinnati, OH 1991.
    Mesoscopic Transport Behavior of 2D Granular Metal Films.

6. **Honors/Awards/Prizes**

1. Brian Patterson's Ph.D thesis "Physical Properties of Granular Metal Thin Films" received the University of Delaware's Wolfe Prize for the best thesis of 1991 in the sciences.

7. **Non-Refereed Publications and Published Technical Reports (the following also appear as contributed talks at the March Meetings of the American Physical Society)**

1. K.M. Unruh, B.M. Patterson, N. Mulders, C. Swann, and J.R. Beamish, Bull. Amer. Phys. Soc. 34, 1033 (1989).
   Preparation and Transport Properties of Reactively Sputtered ZrN_x.

2. J.R. Beamish, K.M. Unruh, and B.M. Patterson, Bull. Amer. Phys. Soc. 35, 830 (1990).
   Electrical Resistivity of Granular Nickel Films.

3. K.M. Unruh, B.M. Patterson, J.R. Beamish, Li Yiping, and G.C. Hadjipanayis, Bull. Amer. Phys. Soc. 35, 830 (1990).
   Magnetic Properties and Magneto-resistance of Granular Metal Films.

4. B.M. Patterson, K.M. Unruh, and J.R. Beamish, Bull. Amer. Phys. Soc. 35, 395 (1990).
   Melting and Freezing Behavior of Small Bi Particles in Granular Bi-SiO_2 Films.

5. Z.-Q. Zhang and P. Sheng, Bull. Amer. Phys. Soc. 35, 830 (1990).
   Theoretical Calculations of Magnetoresistance in Granular Metal Films.

6. M.-Y. Zhou and P. Sheng, Bull. Amer. Phys. Soc. 35, 395 (1990).
   Melting and Thermal Characteristics of Small Particles Embedded in an Elastic Matrix.

7. S.-T. Chui, Bull. Amer. Phys. Soc. 35, 395 (1990).
   Melting of Clusters and Films as a Mass Density Wave Instability.

8. Z.-Q. Zhang and P. Sheng, Bull. Amer. Phys. Soc. 36, 510 (1991).
   Superdiffusive Transport and Metal-Insulator Transition in 2D.

9. P. Sheng and Z.-Q. Zhang, Bull. Amer. Phys. Soc. 36, 658 (1991).
   Mesoscopic Transport Behavior of 2D Granular Metal Films.

8. Graduate Students

1. Brian M. Patterson

Brian Patterson joined the Department of Physics and Astronomy in the fall of 1985 and began working with K.M. Unruh during the summer of 1986. Brian's doctoral thesis "Physical Properties of Granular Metal Thin Films" involved the fabrication, characterization, and experimental study of the thermal and transport properties of granular metal films, and was successfully completed in April 1991. This work was awarded the University's Wolfe Prize for the years best thesis in the sciences. Brian spent two years working as a post-doc with Prof. D. Sellmyer at the University of Nebraska, and is currently working at the Frank J. Seiler Research Laboratory/Materials Division USAF Academy, CO.

2. Mike Allitt

Mike Allitt joined the Department of Physics and Astronomy in the fall of 1986. Following the completion of a Masters Degree (with D.G. Onn) he began working with J.R. Beamish during the summer of 1989. Mike's doctoral thesis "Electronic Conduction in Nickel-Silica Films" focussed on the measurement of the transport properties of granular metal films, and was successfully completed in September 1992. Mike has currently returned to England.

9. Post-Docs

1. Dr. Z.-Q. Zhang

Dr. Zhang began working at Exxon Research and Engineering in January of 1990 and has been working with P. Sheng since that time. While at Exxon he has been working on calculations describing the transport properties of granular metal films. Dr. Zhang is currently a member of the Research Staff at Exxon Research and Engineering.

Summary

1. Papers submitted to refereed journals (and not yet published): none

2. Papers published in refereed journals: 21

3. Books (and sections thereof) submitted for publication: 1 (committed but not yet submitted)

4. Books (and sections thereof) published: 1

5. Patents filed: none

6. Patents granted: 1 (but see section 3 above)

7. Invited presentations: 3

8. Contributed presentations: 16

9. Honors/awards/prizes: 1 (see section 6 above)

10. Non-refereed publications and published technical reports: 9

11. Number of graduate students: 2

12. Number of post-docs: 1